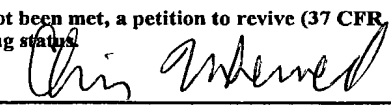


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PCT Applicant's Guide – Volume II – National Chapter – US

US APPLICATION NO. (if known) 10/018557		INTERNATIONAL APPLICATION NO. PCT/GB00/02450		ATTORNEY'S DOCKET NUMBER MPD316	
21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY	
				\$ 890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	8 - 20 =	0	x \$18.00	\$	
Independent claims	4 - 3 =	1	x \$80.00	\$ 84.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$ 974.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	
SUBTOTAL =				\$ 974.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$	
				Amount to be refunded:	\$
				charged:	\$
a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>08-3442</u> in the amount of \$ <u>974.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>08-3442</u> A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: Mr. Russ Stolle Huntsman Corporation Legal Department P. O. Box 15730 Austin, TX 78761			<div style="text-align: center;">  SIGNATURE Christopher J. Whewell NAME 37,469 REGISTRATION NUMBER </div>		

FORM PTO-1390 (REV 11-2000) page 2 of 2

(1 January 2001)

10014520/018557

JC03 Rec'd PCT/PTO 18 DEC 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Hawkins et al.

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Docket # MPD 316

Serial No. unk. (entry into National Stage in US
of PCT/GB00/02450

Filed: concurrently herewith

For: "SURFACTANT EMULSIONS AND
STRUCTURED SURFACTANT
SYSTEMS"

December 18, 2001

Commissioner for Patents
Washington, D.C. 20231

Preliminary Amendment

Sir:

Prior to calculation of the filing fee in the above-captioned matter, please enter
the following amendments to the claims:

5) (AMENDED) A composition according to claim 1 wherein said stabiliser comprises
an ethoxylated C₈₋₂₀ fatty alcohol.

Please add the following new claim:

8 (NEW) A composition according to claim 2 wherein said stabiliser comprises an
ethoxylated C₈₋₂₀ fatty alcohol.

Claim 5 has been amended herein, and new claim 8 added. Support for the added new claim may be found in the multiple-dependent claim 5 originally filed in this case. Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned: **"Version with markings to show changes made"**.

Respectfully Submitted,

A handwritten signature in black ink, appearing to read "Chris Whewell". The signature is fluid and cursive, with the first name "Chris" and last name "Whewell" clearly distinguishable.

Christopher J. Whewell, Reg. No. 37,469
c/o Huntsman Corp.
7114 North Lamar Boulevard
Austin, Tex. 78752
(512) 483-0919

Version with markings to show changes made

5) (AMENDED) A composition according to ~~either of claims 1 and 2~~ claim 1 wherein
said stabiliser comprises an ethoxylated C₈₋₂₀ fatty alcohol.

SURFACTANT EMULSIONS
AND STRUCTURED SURFACTANT SYSTEMS

The present invention relates to non-ionic surfactant emulsions and to the formulation of structured surfactant suspending systems. It is particularly relevant to the formulation of laundry detergents especially those used for industrial and institutional cleaning.

STRUCTURED SURFACTANT

Suspending solids in liquids presents a problem. If the solids differ in density from the liquid they will tend either to sediment or float. Increasing the viscosity of the liquid can retard, but not prevent such separation, and high viscosities are generally undesirable. Colloidal systems, in which the suspended particles are sufficiently small to experience Brownian motion, e.g. less than 1 micron, may be kinetically stable. However the difficulty or undesirability of comminuting some solids to such sizes, and the impossibility of maintaining many of them at this level in the face of crystal growth or agglomeration, limits the use of colloidal suspensions.

Adjusting the density of one phase to match that of the other is usually impracticable. Moreover such systems are almost always temperature-unstable due to differential rates of thermal expansion.

One method of suspension which permits even relatively large particles to be stably suspended is structured surfactant. The term covers systems in which a surfactant mesophase, usually a lamellar or G-phase, alone or more usually interspersed with an aqueous phase, provides a yield stress which is sufficient, when the system is at rest, to immobilise any suspended particles, but which is sufficiently low to allow the system to be poured like a normal liquid. Such systems may display very low apparent viscosities when stirred, pumped or poured and yet be capable of maintaining particles, sometimes of millimetre or larger size, indefinitely in suspension.

Spherulitic phases comprise well defined spheroidal bodies, usually referred to in the art as spherulites, in which surfactant bilayers are arranged as concentric shells. The spherulites usually have a diameter in the range 0.1 to 15 microns and are dispersed in an aqueous phase in the manner of a classical emulsion, but interacting to form a structured system. Spherulitic systems are described in more detail in EP O 151 884.

Expanded G-phases are described in more detail in EP O 530 708. In the absence of suspended matter they are translucent, unlike dispersed lamellar or spherulitic phases which are necessarily opaque. They are optically anisotropic and have shear dependent viscosity. In this they differ from L_1 phases which are micellar solutions and which include microemulsions. L_1 phases are clear, optically isotropic and substantially Newtonian. They are unstructured and cannot suspend solids. Some L_1 phases exhibit small angle x-ray diffraction spectra which show evidence of hexagonal symmetry. Such phases usually have concentrations near the L_1/M phase boundary and may form expanded G-phases on addition of electrolyte.

Most structured surfactant systems require the presence of electrolyte as well as surfactant and water in order to form structured systems capable of suspending solids. However certain relatively hydrophobic surfactants such as isopropylamine alkyl benzene sulphonate can form spherulites in water in the absence of electrolyte. Such surfactants are capable of suspending solids in the absence of electrolyte as described in EP O 414 549.

FLOCCULATION

A problem with the two phase structured surfactant systems, and especially spherulitic systems, is flocculation of the dispersed surfactant structures. This tends to occur at high surfactant and/or high electrolyte concentration. It can have the effect of making the composition very viscous and/or unstable with the dispersed surfactant separating from the aqueous phase.

Certain amphiphilic polymers have been found to act as deflocculants of structured surfactants. One type of deflocculant polymer exhibits cteniform (comb-shaped) architecture with a hydrophilic backbone and hydrophobic side chains or vice versa. A typical example is a random copolymer of acrylic acid and a fatty alkyl acrylate. Cteniform deflocculants have been described in a large number of patents, for example WO-A-9106622.

A more effective type of deflocculant has surfactant rather than cteniform architecture, with a hydrophilic polymer group attached at one end to a hydrophobic group. Such deflocculants are typically telomers formed by telomerising a hydrophilic monomer with a hydrophobic telogen. Examples of surfactant deflocculants include alkyl thiol polyacrylates and alkyl polyglycosides. Surfactant deflocculants are described in more detail in EP O 623 670.

A disadvantage of both surfactant and cteniform deflocculants is that the concentration required to deflocculate to optimum viscosity is critical within fairly narrow limits and varies with temperature. Either too little or too much deflocculant

causes instability and/or excessive viscosity. As a result the deflocculated systems tend to separate if the temperature varies significantly. In particular there is a tendency to form a clear bottom layer on prolonged standing.

One approach to the problem of temperature stability has been to add highly cross linked polyacrylates (see US 5 602 092). These are difficult to disperse in the structure liquid. Our copending application of even date describes the use of certain copolymers to prevent the bottom separation.

APPLICATIONS OF STRUCTURED SURFACTANT

Structured surfactants have been applied to the problems of suspending: water insoluble or sparingly soluble builders in laundry detergent; antifoams and enzymes in laundry detergents and other surfactant systems; abrasives in hard surface cleaners; pesticides and oils in agrochemical preparations (EP O 388 239 and EP O 498 231); rock cuttings in drilling muds (EP O 430 602); dyestuffs in dye bath concentrates and printing inks (EP O 472 089); talcs, oils and other cosmetic ingredients in personal care formulations.

THE PROBLEM

A further kind of temperature instability is often observed with more concentrated structured surfactants especially deflocculated structured surfactants. It typically involves sedimentation of the suspended solid when the composition is stored under warm conditions. We now believe that this separation may be due to a tendency for a phase change in the surfactant from dispersed lamellar or spherulitic to L_2 at elevated temperature.

A similar problem sometimes occurs when attempts are made to prepare non-ionic surfactant emulsions at high concentrations.

We have now discovered that a mixture of a highly ethoxylated non-ionic surfactant and an alkali metal thiocyanate can form highly concentrated emulsions which are temperature stable and also improves the temperature stability of deflocculated structured surfactants. It is readily dispersed in aqueous systems, which are rendered less sensitive to temperature variations thereby.

The mixture is particularly useful for preventing instability in concentrated industrial and institutional detergent. We believe that the mixture inhibits the transition from a G-phase or structured system to an L₂ phase by elevating the phase transition temperature.

THE INVENTION

Our invention, according to a first embodiment provides a mixture of an ethoxylated non-ionic surfactant having an average of from 20 to 100 ethylene-oxy groups per molecule with from 0.1 to 150 parts by weight of a water soluble thiocyanate.

According to a second embodiment the invention provides a concentrated non-ionic surfactant emulsion comprising water, and said mixture in a concentration adapted to form an emulsion or G phase at a temperature below 40°C

According to a third embodiment our invention provides a structured surfactant composition capable of suspending solids which comprises a structuring surfactant, water and, if required, electrolyte in relative proportions adapted to form a dispersed lamellar and/or spherulitic structured surfactant system, capable of forming an L₂ phase at some temperature below 50°C and, optionally sufficient of a deflocculant to inhibit the flocculation of said system characterised in that said composition comprises an effective amount of a phase stabiliser which is a mixture of (i) an ethoxylated non-ionic surfactant having from 20 to 100 ethylene oxy groups and (ii) a water soluble thiocyanate in a relative molar proportion (i):(ii) of from 1 : 200 to 20:1.

Preferably said structuring surfactant consists of a major amount of non-ionic surfactant, typically an ethoxylate with 1 to 15 e.g. 2 to 10 ethylene oxide and optionally a minor amount of anionic and/or amphoteric surfactant. Preferably said water is present in a proportion of from 20 to 60%. Preferably said electrolyte comprises alkali.

- (A) 10 to 50% by weight of the composition of water;
- (B) At least 3% based on the weight of the composition, preferably 4 to 10%, of a structured surfactant comprising more than 50% based on the total weight of surfactant of non-ionic surfactants having a mean HLB of from 8 to 15 and optionally a smaller proportion of anionic and/or amphoteric surfactant;
- (C) At least 10% by weight based on the weight of the composition of builders;

The non-ionic surfactant preferably consists of from 60 to 100% by weight of alkoxylate, preferably ethoxylate or mixed ethoxylate/propoxylate. Typically it comprises alkoxylated C₈₋₂₀, especially C₁₀₋₁₈ natural or synthetic alcohols. The

The composition contains a total of at least 7% by weight of dissolved surfactant desolubilising salts and bases. This includes any dissolved portion of the builder and any alkali required to provide the free alkalinity.

It excludes micelle forming components such as anionic surfactant. The dissolved salts and bases preferably constitute from 10 to 40%, e.g. 15 to 30% by weight of the composition, and sufficient to form a multiphase system in which an aqueous phase is interspersible with a surfactant or surfactant mesophase.

The total free alkali should be sufficient to neutralise at least an equal volume of 0.5 normal HCl. Preferably the free alkalinity is from 0.7 to 2 normal, e.g. 0.8 to 1.5.

We particularly prefer that compositions of the invention contain a deflocculant. The deflocculant may be a polycarboxylate having on or more alkyl groups such as C₈₋₂₀ alkyl thiol polycarboxylate e.g. polyacrylate or polymaleate, or a copolymer of unsaturated carboxylic acid with a C₈₋₂₀ alkyl ester of an unsaturated carboxylic acid e.g. a copolymer of acrylic acid and/or maleic acid with a minor proportion of a C₈₋₂₀ alkyl acrylate and/or alkyl maleate ester. Alternatively it may comprise an alkyl polyglycoside. The alkyl polyglycoside is preferably a polyglucoside and typically has an average degree of polymerisation between 1.3 and 10, more usually 1.5 to 3.

The deflocculant is generally added in an amount sufficient to provide an interspersion of the aqueous phase with the surfactant phase at 25°C, which does not separate within 1 month. This may typically require from 0.5 to 10, more usually 1 to 5%, e.g. 2 to 4.5% by weight based on the weight of the composition. The amount is preferably adjusted to obtain a spherulitic composition comprising surfactant vesicles, usually having a multilamellar or G-phase structure, dispersed in an aqueous phase.

The auxiliary stabiliser may be present in proportions up to 5% by weight, usually 0.01 to 3%, e.g. 0.02 to 2 especially 0.01 to 1. Combinations of two or more auxiliary stabilisers may sometimes be particularly effective.

The detergent compositions of the invention preferably also contain the conventional minor detergent ingredients including antifoams such as silicone antifoam, soil suspending agents such as a carboxymethyl cellulose, optical brighteners, stain removers such as enzymes, bleaches including perborate metaborate mixtures,

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sequestrants such as phosphonates and especially amino phosphonates including aminotrismethylene phosphonate, ethylene diamine tetrakis (methylene phosphonate), diethylene triamine pentakis (methylene phosphonate) and others in the same series, perfumes, colouring, preservatives, corrosion inhibitors, bleach activators such as TAED and/or fabric conditioner.

The aforesaid minor ingredients may all be present in conventional amounts and usually constitute a total of less than 5% by weight of the composition, typically less than 1%. The anionic component of the ionic ingredients may typically be sodium, potassium or a mixture of the two. Potassium is preferred where very high solids contents are desired.

The invention is illustrated by the following example/ in which all proportions are by weight of the 100% material based on the weight of the composition.

	% wt/wt
Potassium thiocyanate	0.5
Optical brightener "TINOPAL" @ CBS/X	0.1
C ₁₂₋₁₄ alkyl (polyglucoside (dip.=1.4)	2.25
Sodium tripolyphosphate	19.0
C ₁₂₋₁₈ alkyl fifty mole ethoxylate	0.4
C ₁₂₋₁₄ branched alkyl seven mole ethoxylate	11.0
Sodium hydroxide	10.0
Water	balance

The above product was an effective industrial and institutional laundry detergent. In the absence of the alkyl polyglycoside the composition was heavily flocculated and underwent rapid separation. In the absence of the potassium thiocyanate and/or the fifty mole ethoxylate the product separated at temperatures above 30°C.

CLAIMS

1. A mixture of an ethoxylated non-ionic surfactant having an average of from 20 to 100 ethylene-oxy groups per molecule with from 0.1 to 150 parts by weight of a water soluble thiocyanate.
2. A concentrated non-ionic surfactant emulsion comprising water, and said mixture in a concentration adapted to form an emulsion or G phase at a temperature below 40°C.
3. A structured surfactant composition capable of suspending solids which comprises a structuring surfactant, water and, if required, electrolyte in relative proportions adapted to form a dispersed lamellar and/or spherulitic structured surfactant system, capable of forming an L₂ phase at some temperature below 50°C and, optionally sufficient of a deflocculant to inhibit the flocculation of said system characterised in that said composition comprises an effective amount of an phase stabiliser which is a mixture of (i) an ethoxylated non-ionic surfactant having from 20 to 100 ethylene oxy groups and (ii) a water soluble thiocyanate in a relative molar proportion (i):(ii) of from 1 : 200 to 20:1.
4. A composition according to claim 3 wherein said structuring surfactant comprises a major amount of a non-ionic surfactant and a minor amount of anionic and/or amphoteric surfactant.
5. A composition according to either of claims 1 and 2 wherein said stabiliser comprises an ethoxylated C₈₋₂₀ fatty alcohol.

7. A composition according to claim 6 wherein thiocyanate is potassium thiocyanate.

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International Bureau

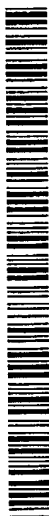


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(54) Title: SURFACTANT EMULSIONS AND STRUCTURED SURFACTANT SYSTEMS

(57) Abstract: A mixture of an ethoxylated non-ionic surfactant having an average of 20 to 100 ethylene-oxy groups per molecule with from 10 to 150 parts by weight of a water soluble thiocyanate stabilises non-ionic emulsions and in particular deflocculated non-ionic structured surfactant systems by raising the lamellar/L₂ phase transition temperature.

DECLARATION FOR PATENT APPLICATION

As an undersigned inventor, I hereby declare that:

My residence, post office address and country of citizenship are as stated directly below my name.

I believe (check one) ☒ I am the original, first and sole inventor
☐ I am a joint inventor and the below named inventors are the
original and first inventors

of the subject matter which is claimed and for which a patent is sought on the invention entitled
"SURFACTANT EMULSIONS AND STRUCTURED SURFACTANT SYSTEMS"

(Attorney Docket **MPD316**),

the specification of which

(check one) ☐ is attached hereto.

☒ was filed on June 22, 2000

as Application Serial No. PCT/GB00/02450

and was amended on _____.

(if applicable)

I further declare that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office (hereinafter "the Office") all information known to me to be material to patentability of the subject matter which is claimed as defined in 37 C.F.R. §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119 of any foreign application(s) for patent or inventor's certificate indicated below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)		Day/Month/Year Filed	Priority Claimed	
Number	Country		Yes	No
<u>9914674.8</u>	<u>Great Britain</u>	<u>24 June 1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
_____	_____	_____	<input type="checkbox"/>	<input type="checkbox"/>

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose to the Office all information known to me to be material to

patentability as defined in 37 C.F.R. §1.56, which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status (patented, pending, abandoned)

Address all telephone calls to Christopher J. Whewell at telephone number 512 483 0919.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and may jeopardize the validity of the application or any patent issued thereon.

1-00 Full name of inventor John Hawkins

Inventor's Signature [Signature] 31-1-2002
Date

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